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CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

MINES BRANCH

OTTAWA

MINERAL SCIENCES DIVISION

INTERNAL REPORT MS-65-117

A SPECTROPHOTOMETRIC STUDY OF HEXA-, PENTA- AND TETRA-COORDINATED HALOGENOCOPPER(II) COMPLEXES IN ACETONE-HYDROHALIC ACID MIXTURES

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(Prepared for publication in Canadian Journal of Chemistry)

December 2, 1965

90-04641/

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ABSTRACT

A spectrophotometric study of the Cu(II)-acetone-hydrochloric (hydrobromic) acid systems has revealed that at relatively high ratios of halide: copper there is an equilibrium between octahedrally and tetrahedrally coordinated tetrahalogenocopper(II) complexes with a probable five-coordinate intermediate. The tetrahedral species is favored at the highest ratios. Ligand field bands of octahedral monohalogenocopper(II) complexes and, in the visible, a charge transfer band of the octahedral complex, $\left[CuCl_4(ac)_2\right]^{2-}$, have been identified. The results of the present work point to the important role of the solvent in determining the geometries and absorption spectra of the complexes, a factor that seems to have been misinterpreted by some previous workers.

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INTRODUCTION

It is known that the tetrahalogenocopper(II) ion exists as a tetragonally distorted tetrahedron in crystalline solids such as Cs_2CuCl_4 (1), $\left[Ph_3MeAs\right]_2CuCl_4$ and $\left[Ph_3MeAs\right]_2CuBr_4$ (2), in molten chlorides (3, 4) and in certain aqueous and organic solvent media (5, 6). The structural information on the solids has been obtained largely through x-ray diffraction work and, on the solutions (including melts), by comparisons of the absorption spectra of the complexes in the two states of matter. In general, however, the absorption spectra of solutions of the halogen complexes of Cu(II) have been difficult to interpret because of "solvent effects" (7) and because of charge transfer bands arising in the visible region (8). In several cases these problems have led to the proposal of complexes that the present author finds difficult to reconcile with his own findings.

As a basis for discussion of previous work, it can be recalled that 3d transition metal complexes in solution exhibit absorption bands from the near ultraviolet to the near infrared region of the energy spectrum. Bands in the high energy region, with absorption coefficients, ϵ_{max}, $>\sim 500$ 1/mole-cm and oscillator strengths, f, $>\sim 10^{-2}$, are probably of the charge transfer type (ligand $\rightarrow$ metal), while bands in the visible to near infrared with $\epsilon_{max} <\sim 500$ 1/mole-cm and $f <\sim 10^{-2}$ are the ligand field d-d bands.

Cu(II) has a d^9 configuration, which in a cubic field, gives rise to a single band due to the transition $T_{2g} \rightarrow E_g$. In an approximately octahedral field such as that in $Cu(OH_2)_6^{2+}$, this transition occurs at 12,500 cm^{-1} (800 mμ) (9). In a tetrahedral field, the transition should occur at a frequency less than 10,000 cm^{-1} because, theoretically, $\Delta_{tetr} \simeq 4/9$

Δ_{oct} (10) (where Δ symbolizes d-orbital splitting). Felsenfeld (11), using theoretical considerations based on a tetrahedral model for $CuCl_4^{2-}$, showed that the complex should have a d-d band at 5768 cm^{-1}.

Helmholz and Kruh (1) have shown that $CuCl_4^{2-}$ in crystalline Cs_2CuCl_4 is a flattened tetrahedron. These workers compared the absorption spectra (in the 10,000 - 45,000 cm^{-1} region) of a mull of powdered Cs_2CuCl_4 and that of an aqueous solution of cupric chloride, and concluded that the structure of the aqueous ion was not the same as that in the crystal. Both spectra obtained by Helmholz and Kruh show charge transfer bands ($f > 2 \times 10^{-2}$) above 20,000 cm^{-1}, but the only d-d band resolved was that of the solution at about 13,000 cm^{-1} (~770 mμ). It will be evident later in the paper that this band probably should have been drawn with a maximum near 11,000 cm^{-1}; but in either case, according to the criteria outlined above, one may be led to conclude that copper probably did not exist in the solution mainly as a tetrahedral complex. It may be noted however, that in a theoretical paper on the intensities of spectral bands in tetrahedral complexes, Ballhausen and Liehr (12) state that they considered the "$CuCl_4^{2}$" complex in solution to be rigorously tetrahedral.

Antipova-Karataeva and co-worker (7) studied the spectra of solutions of cupric chloride in acetone and noted a relatively intense band at about 21,000 cm^{-1} (475 mμ) which they attributed to a solvated complex of low symmetry and implied that it contained less than four chlorines per copper. Because of the attempted structure assignment, it would appear that Antipova-Karataeva and co-worker considered this maximum to be due to a d-orbital transition because charge transfer bands do not readily permit such assignments.

Gazo (13) also observed the maximum at 21,000 cm^{-1} and showed

that it was due to a tetrachloro complex; however, he did not identify the band as being either charge transfer or d-d in character. It will be shown later in this paper that it is a charge transfer band.

Furlani and Morpurgo (6) obtained the spectra of nitromethane solution of certain salts of the general formula, R_2CuCl_4, and under some conditions these show an absorption peak at 21,900 cm^{-1}. Furlani and Morpurgo attribute this charge transfer band to a "solvolysis product" and imply that the complex contained less than four chlorines per copper--a conclusion similar to that of Antipova-Karataeva and co-worker.

In nitromethane solutions of R_2CuX_4 (X = Cl or Br) containing excess X^-, the spectra measured by Furlani and Morpurgo show broad bands with maxima at 8000 - 9000 cm^{-1} and these are considered to be the d-d bands of pseudo-tetrahedral tetrahalogeno complexes. However, in the spectra of similar solutions not containing excess halide, maxima appear at 11,500 - 12,000 cm^{-1} and Furlani and Morpurgo assign these to distorted square planar solvolysis products, i.e. di- and/or tri-halide species such as CuX_2L_2.

Gill and Nyholm (2) studied the complexes $\left[Ph_3MeAs\right]_2 CuCl_4$ and $\left[Ph_3MeAs\right]_2 CuBr_4$ but did not publish their crystal or solution spectra. However, they did indicate that they found absorbance maxima for "$CuCl_4^{2-}$" and "$CuBr_4^{2-}$" in nitromethane solutions at 11,200 and 11,500 cm^{-1} respectively, with corresponding ϵ_{max} values of 88 and 122 1/mole-cm. Using the arguments presented earlier, the above spectral data suggest that the two complexes, in solution, were of approximately octahedral symmetry. Gill and Nyholm suggest that in nitromethane solution, a tetrahedral arrangement is not at all certain for their tetrahalogen complexes.

Barnes and Hume (5) have established the existence of the

distorted tetrahedral $CuBr_4^{2-}$ ion in both aqueous and organic solvents and this has been considered to be the only example of such a geometry for Cu(II) complexes in liquid solutions (4). According to Barnes and Hume, the d-d band of the purple tetrabromo complex has its maximum at 9,100 cm^{-1} (1100 mμ) with ϵ_{max} = 160, both parameters in the accepted range for tetrahedral (approximately) complexes.

Barnes and Hume also investigated a green complex which, in acetone solutions, was found to have its d-d band at about 11,400 cm^{-1} (880 mμ) with ϵ_{max} = 160. Apparently the green complex had been studied previously by Yatsimirskii and Malkova (14) who concluded that it was $CuBr_4^{2-}$. However, Barnes and Hume consider the species to be the five-coordinate entity, $CuBr_3^-$.2 solvent. As we will see later, it is probable that it is an octahedrally coordinated tetrabromo complex.

From the foregoing it is evident that further experimental work is required to elucidate the spectra and structure of the halogenocopper(II) complexes, especially in coordinating solvents such as acetone. The present paper describes studies directed to that end.

It will be shown that in acetone solutions, containing an excess of Cl^- or Br^-, an equilibrium exists between octahedral and tetrahedral (both distorted) tetrahalogenocopper(II) complexes, the tetrahedral arrangement being favored in solutions having the highest halide ion activity. The experimental evidence, although not conclusive, strongly suggests the existence of a five-coordinate (probably pentachloro) intermediate in the octahedral-tetrahedral equilibrium.

The important role of solvent molecules as "primary" ligands is indicated in the present study where the six-coordinate complexes are considered to be $\left[CuCl_4(ac)_2\right]^{2-}$ and $\left[CuBr_4(ac)_2\right]^{2-}$. Information on

octahedral monohalogenocopper(II) species has been obtained and it seems that these are considerably more stable than the higher halogeno octahedral complexes.

EXPERIMENTAL

Stock Solution of $CuCl_2.2H_2O$ in Acetone

This was prepared by dissolving an accurately weighed quantity of analyzed (37.5% Cu) reagent grade $CuCl_2.2H_2O$ in the required volume of reagent grade acetone. Recent studies in this laboratory have shown that in such solutions the coordination sphere of the dissolved copper species changes through the formation of monochloro complexes. For that reason freshly prepared solutions only were used in the present studies.

Stock Solution of $Cu(ClO_4)_2$ in Acetone

This was prepared by dissolving high-purity copper turnings in concentrated nitric acid, evaporating the resulting solution just to dryness and then treating the salt with several ml of concentrated perchloric acid. The solution was evaporated until copper perchlorate had crystallized and nearly all free perchloric acid had been driven off. After cooling, the residue was treated with acetone and several drops of concentrated perchloric acid (just sufficient to produce a clear solution) and diluted to a known volume with acetone.

Apparatus

All spectrophotometric measurements were made with a Beckman DK-2 recording spectrophotometer equipped with matched 1-cm cells.

Experimental Procedure

Most sample solutions were prepared by mixing aliquots of the appropriate copper stock solution with aliquots of either concentrated hydrochloric or hydrobromic acids, or of solutions of known concentration of each acid in acetone. The resulting mixtures were diluted to 25 ml with acetone and, as quickly as possible, cooled to room temperature and examined spectrophotometrically. In obtaining the spectra, copper-free reference solutions containing all ingredients in the same concentration as the corresponding samples were used.

Because of the high absorbance of the solvent medium, the spectra could not be examined above approximately 31,000 cm^{-1} ($\sim$320 mμ) or below approximately 6,000 cm^{-1} ($\sim$1700 mμ).

Extinction coefficients (ϵ_{max}) were calculated using total copper concentrations.

RESULTS AND DISCUSSION

Chlorocopper(II) Complexes in Acetone-Hydrochloric Acid Solutions

Monochlorocopper(II) Complex

From the spectra shown in Fig. 1 it is evident that, as the ratio of the total molar concentrations of Cl^- to Cu^{2+} is increased from zero to about 1.3, there is a gradual increase in the intensity of the d-d band and a shift of the band maximum from 12,500 to about 12,200 cm^{-1} (820 mμ). In the mole ratio range 1.3 to 2.5 (not shown), the intensity increase continues and there is sudden shift of the maximum to 11,500 cm^{-1} (870 mμ), at which value it remains constant up to a ratio of approximately 20:1 (see B of Fig. 2).

Absorbance data from Fig. 1, together with that from additional

spectra, have been plotted against $\left[Cl^-\right]/\left[Cu^{2+}\right]$ in Fig. 3(a) and from this it is clear that Cu(II) and chlorine are present in a 1:1 ratio in the complex with d-d band maximum at 12,200 cm^{-1} (820 mμ).

In the interpretation of these spectral changes, it is assumed that spectrum A in Fig. 1 is that of a distorted (Jahn-Teller effect) octahedral complex $\left[Cu(OH_2)_4(ac)_2\right]^{2+}$ (where ac = acetone). Friedman and Plane (15) have shown that such a complex is present in acetone solutions of copper perchlorate containing small amounts of water. Since no free water was added to the initial system in the present work, it is possible that more than two molecules of acetone were present in the inner coordination sphere. However, the acetone used may well have contained as much as 0.05% water and because ϵ_{max} = 27 l/mole-cm at 12,500 cm^{-1} is similar to the value given by Friedman and Plane for $\left[Cu(OH_2)_4(ac)_2\right]^{2+}$, it is reasonable to assume that this is the complex responsible for the 12,500 cm^{-1} band. It is worth noting here that $\left[Cu(OH_2)_4(ac)_2\right]^{2+}$ has its d-d band maximum at the same energy as $Cu(OH_2)_6^{2+}$ because of the similar ligand fields of acetone and water (15).

From the above considerations it can be concluded that the monochlorocopper(II) complex is probably $\left[CuCl(OH_2)_3(ac)_2\right]^+$, or in the extreme, $\left[CuCl(ac)_5\right]^+$. Because acetones are preponderant in the system, it is felt that water molecules in the coordination sphere are replaced preferentially by chlorines. The decrease of approximately 300 cm^{-1} in Δ_{oct} accompanying the introduction of a chlorine into the coordination sphere is consistent with its position in the spectrochemical series.

At energies higher than approximately 20,000 cm^{-1} certain spectra in Figs. 1 and 2 show bands, which, because of their intensity (and energy), are considered to be of the charge transfer type. Because these bands arise

with chloride ligandcy it is reasonable to assume that they are due to electronic transitions from ligand orbitals to orbitals centered on coppers. It is to be noted that the band at approximately 21,000 cm^{-1} (475 mμ) is not apparent until $\left[Cl^-\right]/\left[Cu^{2+}\right]$ exceeds 1:1; this band will be discussed more fully later in the paper.

Equilibrium Between Octahedral and Tetrahedral Tetrachlorocopper(II) Complexes with Possible Five-Coordinate Intermediate

Octahedral Complex

Fig. 3(b) shows the variation in absorbance at 11,500 cm^{-1} (see also B of Fig. 2) with the ratio $\left[Cl^-\right]/\left[Cu^{2+}\right]$; the plot indicates that the absorbing species contains four chlorines per copper. There seems to be little doubt that the complex is approximately octahedral and thus it can be formulated as $\left[CuCl_4(ac)_2\right]^{2-}$. From Fig. 1 it is evident that Δ_{oct} of this species is 1000 cm^{-1} smaller than that of $\left[Cu(OH_2)_4(ac)_2\right]^{2+}$, i.e. an average decrease of 250 cm^{-1} for each chlorine.

The band maxima between 12,200 and 11,500 cm^{-1} in Fig. 1 are probably due to octahedral complexes containing two and three chlorines per copper.

The oscillator strength, f, of the 11,500 cm^{-1} transition is approximately 10^{-3}, as calculated from the expression $f = 4.6 \times 10^{-9} \epsilon_{max} \nu_{\frac{1}{2}}$ ($\nu_{\frac{1}{2}}$ is the band width where $\epsilon_\nu = \frac{1}{2} \epsilon_{max}$) (16), and this is appropriate for an octahedral complex (cf. $\sim 7 \times 10^{-4}$ for $\left[CuOH_2)_4(ac)_2\right]^{2+}$).

The value of the oscillator strength, and the relatively high degree of symmetry of the band at 11,500 cm^{-1} are indicative of a complex of high octahedral symmetry, one in which the four halide ions bind in a square plane. This is in accord with previous findings that singly charged ligands are similarly bound (17). Close examination of the spectrum

of $\left[CuCl_4(ac)_2\right]^{2-}$ reveals evidence of minor shoulders, probably manifestations of Jahn-Teller splitting.

Tetrahedral Complex

Spectrum B in Fig. 2 shows that even at relatively low values of $\left[Cl^-\right]/\left[Cu^{2+}\right]$, an appreciable proportion of the copper in the system is present as a species with an absorbance maximum at approximately 8,900 cm^{-1} As indicated by the mole ratio plot in Fig. 3(c), this band is also due to a 4:1 complex. The d-orbital splitting interval, Δ, for this complex is appreciably less than that for the octahedral species described above, but it is larger than that calculated ($\sim$5,800 cm^{-1}) from theoretical considerations (11). It is known (1, 3, 6) that in certain systems $CuCl_4^{2-}$ is distorted, tending toward a planar structure; because of this distortion a Δ value greater than Δ_{tetr} is to be expected for the complex. Therefore, it is reasonable to assume that the 8,900 cm^{-1} band is due to a complex having distorted tetrahedral symmetry. The change in absorbance at 8,900 and 11,500 cm^{-1} with variation in chloride ion concentration strongly suggests the existence of an equilibrium between the tetrahedral and octahedral species.

The asymmetry of the 8,900 cm^{-1} band (see D, especially in Fig. 2) indicates that there is one, or more components at lower energies - the result of factors that cause further splitting of the d-orbital energy levels. As we will see later, the d-d band of tetrahedral $CuBr_4^{2-}$ (G and H in Fig. 2) in acetone media can be resolved into two peaks and there is reason to believe that the spectrum of $CuCl_4^{2-}$ would be analagous if it could be examined at sufficiently low energy. By extrapolation of spectrum D it is estimated that the low energy peak would lie between 5500 and 6000 cm^{-1}. Such a spectrum would be very similar to that of $CuCl_4^{2-}$ in Cs_2CuCl_4

at room temperature, in which Ferguson (18) found two major peaks at 9050 and 5550 cm^{-1}. (At 20°K, Ferguson observed four d-d bands for the complex and made transition assignments for each.)

Close inspection of spectra B, C and D of Fig. 2 reveals that the band maximum near 9,000 cm^{-1} (1,100 mμ) shifts slightly to higher energies in solutions that are relatively concentrated with respect to hydrochloric acid (i.e. >~2M). This behaviour is to be expected because such solutions contain enough water (from 12M HCl) for it to compete effectively with chlorines for sites in the complex and thus the "blue shift" possibly represents the formation of a distorted tetrahedral complex having fewer than four chlorines per copper.

Evidence for Five-Coordinate Intermediate

At first glance, the shoulder in both spectra C and D of Fig. 4 appears to be a "remnant" of the d-d band of $\left[CuCl_4(ac)_2\right]^{2-}$. However the maximum of the shoulder in D lies approximately 800 cm^{-1} lower than that of the octahedral complex and therefore it seems necessary to invoke the existence of an additional complex to account for a shift of this magnitude.

From Fig. 5 (the calculation of the values on the abscissa to be explained later) it is evident that when the total concentration of hydrochloric acid in the solution is 1 - 1.3M (i.e. when $\left[Cl^-\right]/\left[Cu^{2+}\right]$ is 120 - 160, approximately 30% of Cu(II) is present as the octahedral species $\left[CuCl_4(ac)_2\right]^{2-}$ with d-d band maximum at 11,500 cm^{-1}. The limiting value of the absorbance for this band is 0.89 (Figs. 2 and 3(b)) and therefore, in the mole ratio range mentioned above, it would be expected that the absorbance at the band maximum would be approximately 0.3 in the absence of other species absorbing appreciably at the same energy. However, the absorbance of the shoulder at 10,500 - 11,000 cm^{-1} is over twice as high and this can be accounted for by the presence of an additional complex of appreciable intensity.

It is tempting to postulate the existence of a five-coordinate complex (possibly pentachloro) as an intermediate in the structural transition from approximately octahedral $\left[CuCl_4(ac)_2\right]^{2-}$ to distorted tetrahedral $CuCl_4^{2-}$.

The $CuCl_5^{3-}$ ion has been identified in certain crystalline solids and its absorption spectrum shows a charge transfer band at approximately 27,000 cm^{-1} (19) and a d-d band at 10,400 cm^{-1} (20), the latter being comparable to the shoulder of spectrum D at 10,700 cm^{-1}.

Of considerable interest are the spectra of solutions of $CuCl_2.2H_2O$ in 12M HCl shown in Figs. 2(I) and 4(S). These show respectively, a charge transfer band at approximately 27,000 cm^{-1} and a d-d band at approximately 10,500 cm^{-1}; thus one is led to conclude that, in the solutions studied, an appreciable proportion of the copper probably existed as $CuCl_5^{3-}$. The asymmetry of the d-d band may be due to a "contribution" from the distorted $CuCl_4^{2-}$.

Charge Transfer Bands

Charge transfer bands in the spectra of the tetrachlorocopper(II) complexes in the visible to near ultraviolet region are shown in Fig. 2 (E and F).

The mole ratio plot in Fig. 3(d) indicates that the complex responsible for the 21,000 cm^{-1} (475 mμ) band has four chlorines per copper and this is in agreement with the findings of Gažo (13) but not those of Furlani and Morpurgo (6). Because the band rises and falls in concert with the d-d band at 11,500 cm^{-1}, it can be concluded that it is due to the complex $\left[CuCl_4(ac)_2\right]^{2-}$. From the estimated limiting value of the absorbance (~0.42) and the total copper concentration indicated in Fig. 3(d), ϵ_{max}, at 21,000 cm^{-1}, is calculated to be approximately 2,100 l/mole-cm.

Using this value together with absorbance readings at various hydrochloric acid concentrations, the proportion of the total copper in the system that is present as $\left[CuCl_4(ac)_2\right]^{2-}$ has been calculated from $\frac{\text{absorbance}}{2100\left[Cu^2\right]_{\text{total}}}$ Figure 5 shows how this varies with the hydrochloric acid concentration.

Figure 2 shows that the 21,000 cm^{-1} band virtually disappears at high Cl^- concentrations and is replaced by a new charge transfer band at approximately 25,000 cm^{-1}. The new band is similar to, but of slightly lower energy, than that observed for chlorocopper(II) complexes at very high Cl^- concentration (8-12M) in aqueous solutions. It is probable that the band is analagous to that found at 24,800 cm^{-1} by Ferguson (18) in the spectrum of tetrahedral $CuCl_4^{2-}$ in Cs_2CuCl_4.

The wedge-shaped band with maximum between 30,000 and 32,000 cm^{-1} (and which appears to contain several components) also seems to be associated with the octahedrally coordinated complexes, for it appears at low $\left[Cl^-\right]/\left[Cu^{2+}\right]$ ratios and decreases in intensity in accord with the 21,000 and 11,500 cm^{-1} bands of $\left[CuCl_4(ac)_2\right]^{2-}$ at high ratios.

Bromocopper(II) Complexes in Acetone-Hydrobromic Acid Solutions

A brief spectrophotometric study was made of bromocopper(II) complexes formed in the copper perchlorate-acetone-hydrobromic acid (8.2M) system. Using experimental techniques similar to those described earlier, the following are some of the findings and their interpretation:

(a) When $\left[Br^-\right]/\left[Cu^{2+}\right]<\sim 1$, a relatively stable octahedrally coordinated complex, $\left[CuBr(OH_2)_3(ac)_2\right]^+$, is formed. The d-d band of this complex has its maximum at 12,000 cm^{-1} (835 mμ) and $\epsilon_{max}\sim 60$ l/mole-cm.

(b) Rapid reduction of Cu(II) to Cu(I) by Br^- occurs when $\left[Br^-\right]/\left[Cu^{2+}\right]$ is in the range 1 - 150 (i.e. when $\left[HBr\right]$=0.01 - 1.5M) and thus it is possible to obtain only semi-quantitative spectral data, at best. However, the

transient spectra of the green solutions produced under these conditions show a low-intensity band between 11,800 and 11,100 cm^{-1} (~845 - 900 mμ). By analogy to the chloride system, it is felt that absorption in this region is due to octahedral species containing from two to four bromines per copper and these complexes are unstable with respect to cuprous complexes (probably tetrahedral).

Barnes and Hume (5) found a band maximum at about 11,400 cm^{-1} in the spectrum of the green species in acetone solutions and they ascribed this band to the complex "$CuBr_3^-$.2 solvent". In view of the present findings, it seems more probable that the complex is $\left[CuBr_4(ac)_2\right]^{2-}$.

(c) At high hydrobromic acid concentrations (1.5 to at least 3.5M) a purple complex, presumably tetrahedral $CuBr_4^{2-}$ (5), is formed. Compared with the octahedral 1:2, 1:3 and 1:4 bromo complexes the purple species seems to be relatively stable to reduction by Br^-.

The d-d bands (G and H of Fig. 2) of the $CuBr_4^{2-}$ complex show two peaks that lie somewhat closer together in acetone-hydrobromic acid solutions than in 8.2M hydrobromic acid. The peaks are similar to those observed in the spectrum of $CuCl_4^{2-}$ in Cs_2CuCl_4 (18).

(d) The spectra of acetone solutions of Cu(II) containing hydrobromic acid in intermediate concentrations reveal maxima at both approximately 11,000 and 8,400 cm^{-1} thus suggesting that the system is directly analogous to that of the chlorocopper(II) complexes, i.e. there is an equilibrium between octahedral and tetrahedral tetrabromocopper(II) complexes.

It is noteworthy that the ligand field bands of the octahedral and the high-energy component of the band of tetrahedral bromocopper complexes appear at lower energies than those of the corresponding chloro complexes and this is to be expected from the position of the halogens in the

spectrochemical series.

Comparison of Spectra of Halogenocopper(II) Complexes in Acetone Solution with those in Chloride Melts and Crystalline Solids

For comparison purposes, spectral and structural data from the present study and from various other sources, previously cited, are listed in Table I.

The results of the present study, indicating an equilibrium between six- and four-coordinate tetrachloro (bromo) Cu(II) complexes in an acetone medium, are similar to those of Gruen and McBeth (3) who studied the absorption spectra of Cu^{2+} in LiCl-KCl melts. However, Gruen and McBeth did not find evidence for, or postulate the presence of, a five-coordinate intermediate.

The halide ion activity in acetone-concentrated hydrochloric acid mixtures, having a final concentration of approximately 1 - 4M for the acid, is comparable to that in chloride melts such as those used by Gruen and McBeth. For example, these workers estimate that the ratio of the concentrations of the tetrahedral and octahedral chlorocopper species in a LiCl-KCl melt at 1000°K is 2.2. In the present work (Fig. 4) this ratio corresponds to a solution in which the total molar concentration of hydrochloric acid is 1 - 1.5M.

General Discussion of Proposed Equilibrium Between Four-, Five- and Six-Coordinate Complexes

The experimental evidence suggests that, in acetone-hydrohalic acid mixtures, an equilibrium exists between four-, five- and six-coordinate halogenocopper(II) complexes that may be expressed by:

$$\left[CuX_4(ac)_2\right]^{2-}_{oct} + X^- \rightleftharpoons CuX_5^{3-} + 2ac$$

$$CuX_5^{3-} \rightleftharpoons \left[CuX_4\right]^{2-}_{tetr} + X^-, \text{ where X = Cl or Br.}$$

TABLE I

Correlation of spectral data and structure of chloro- and bromocopper(II) complexes

Absorbing Species	Maximum of d-d band cm^{-1}	Approx. ϵ_{max} 1/mole-cm.	Structure	Source
$CsCd_{1-x}(Cu)_2Cl_3(CuCl_6^{4-})$	12,400	---	distorted octahedron	(3)
$\left[Cu(OH_2)_4(ac)_2\right]^{2+}$	12,500	27	"	present work
$\left[CuCl(OH_2)_3(ac)_2\right]^{+}$	12,200	65	"	"
$\left[CuBr(OH_2)_3(ac)_2\right]^{+}$	12,000	60	"	"
$\left[CuCl_4(ac)_2\right]^{2-}$	11,500	110	"	"
$\left[CuBr_4(ac)_2\right]^{2-}$	~11,000	---	"	"
$CuBr_3^-$.2 solvent (acetone)	~11,400	160	trigonal bipyramid	(5)
$CuCl_4^{2-}$ in LiCl-KCl at 800°C	9,000	---	distorted tetrahedron	(3)
$CuCl_4^{2-}$ in Cs_2CuCl_4	9,050 and 5,550		"	(18)
$CuCl_4^{2-}$ in acetone - HCl	8,900 and 5,500 - 6,000	130 ~100	"	present work
$CuBr_4^{2-}$ in acetone - HBr	8,400 and 6,900	100-150 100-150	"	"
$CuBr_4^{2-}$ in various coordinating solvents	9,100	160	"	(5)
$\left[R_4N\right]_2CuBr_4$	9,100		"	(5)
$\left[Co(NH_3)_6\right]\left[CuCl_5\right]$	10,400 and 8,200		trigonal bipyramid	(19)
$CuCl_5^{3-}$ in acetone - HCl (tentative)	~10,700			present work

Thus it is apparent that at high halide ion concentration, such an equilibrium is shifted toward the intermediate pentachloro complex from which the final tetrahedral species is formed.

At low $\left[X^-\right]/\left[Cu^{2+}\right]$, octahedral ligand field stabilization energy is probably of major importance in deciding the geometry of the complex. However, at higher ratios, solvent molecules (acetone) can probably no longer compete effectively for sites in the octahedral coordination sphere and they tend to be replaced by halide ions. Because of their relatively large size, the ions repel each other strongly and this induces a structural re-arrangement, possibly first to a trigonal bipyramid and then to a distorted tetrahedron in which the ligands are at a more electrostatically favorable separation.

Previously it was mentioned that octahedral bromocopper(II) complexes containing more than one bromine are unstable with respect to reduction to cuprous species. The reduction process also results in the formation of a tetrahedral structure (21), in which Cu(I) exists as a d^{10} ion with all electrons occupying relatively stable orbitals. It is probable that charge transfer processes in $\left[CuBr_4(ac)_2\right]^{2-}$ are more efficient than in $\left[CuCl_4(ac)_2\right]^{2-}$ since the lowest energy charge transfer bands observed for these complexes appear at approximately 15,000 and 21,000 cm^{-1} respectively; and this accounts for the greater stability of the octahedral tetrachlorocopper(II) species with respect to reduction of copper.

ACKNOWLEDGMENT

The author wishes to express appreciation to Dr. P.G. Manning for his sincere interest and for his valuable advice during the course of this work.

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CAPTIONS AND LEGENDS FOR FIGURES

Fig. 1. Spectra of octahedral complexes

$[Cu]_{Total} = 3.76 \times 10^{-3}$M

	$[Cl^-]/[Cu^{2+}]$
A	0
B	0.64
C	0.96
D	1.28
E	1.92
F	3.20

Fig. 2. Spectra of tetrahedral complexes

	$[Cu^{2+}]_{Total}$	$[Cl^-]/[Cu^{2+}]$
A	8×10^{-3} M	2
B	"	8
C	"	120
D	"	610
E	2×10^{-4}	26)note change of
F	"	12,000)scale for ϵ_{max}

G $>4 \times 10^{-3}$M, acetone solution, 3.3M in HBr.

H 2.5×10^{-3}M, 8.2 m HBr (aqueous).

I 2×10^{-4}M, $CuCl_2.2H_2O$ in 12 M HCl.

Fig. 3. Mole ratio plots.

Fig. 4. d-d bands of hexa-, penta-, and tetra-coordinated species.

$[Cu^{2+}]_{Total} = 8 \times 10^{-3}M$

	$[Cl^-]/[Cu^{2+}]$
A	8
B	62
C	120
D	154
E	$2 \times 10^{-3}M$ solution of $CuCl_2.2H_2O$ in 12M HCl

Fig. 5 Fraction of total copper present as $CuCl_4(ac)_2^{2-}$.

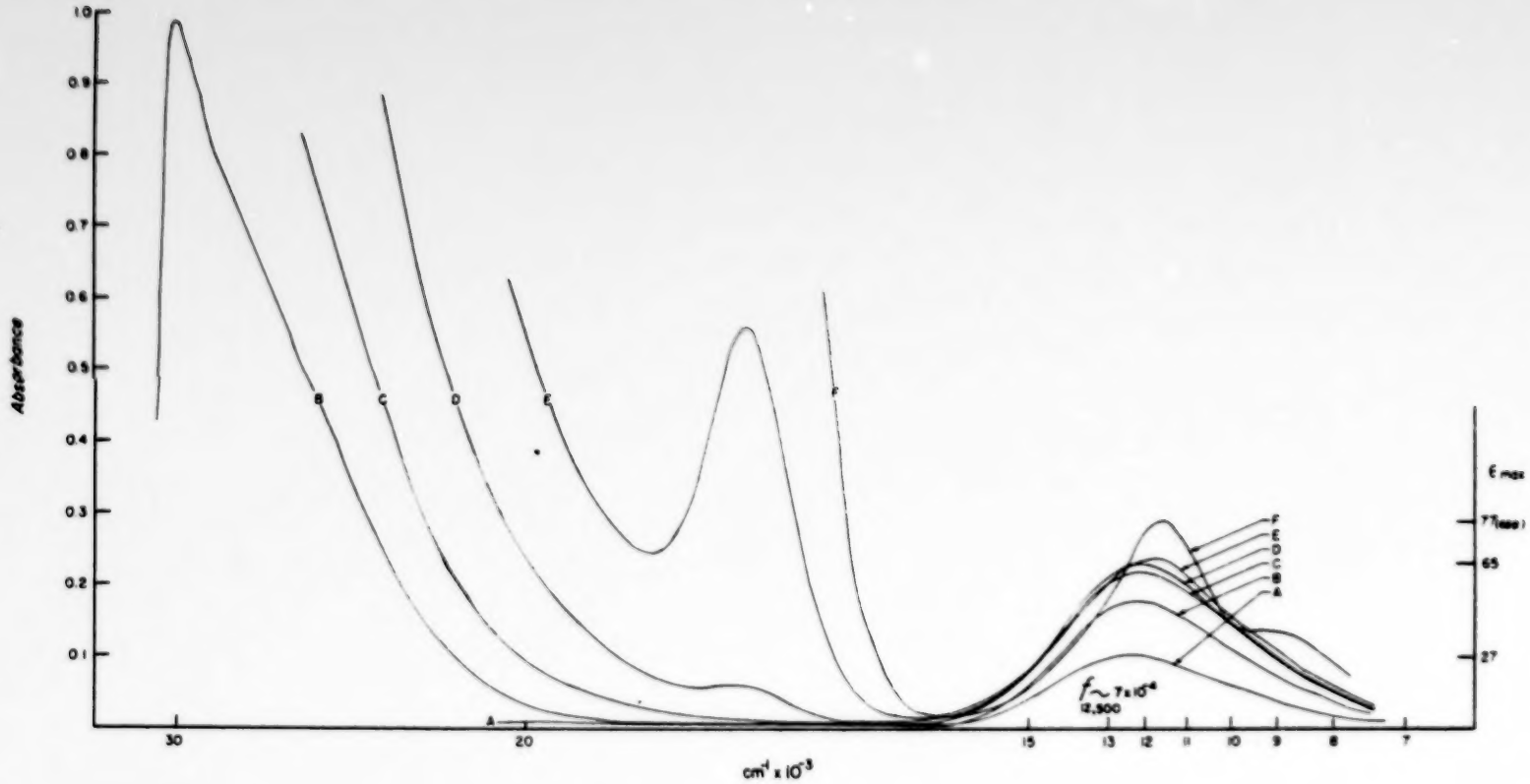

Figure 1 - Spectra of octahedral complexes

$Cu_{Total} = 3.76 \times 10^{-3}M$

Cl^- / Cu^{2+}	
A - 0	D - 1.28
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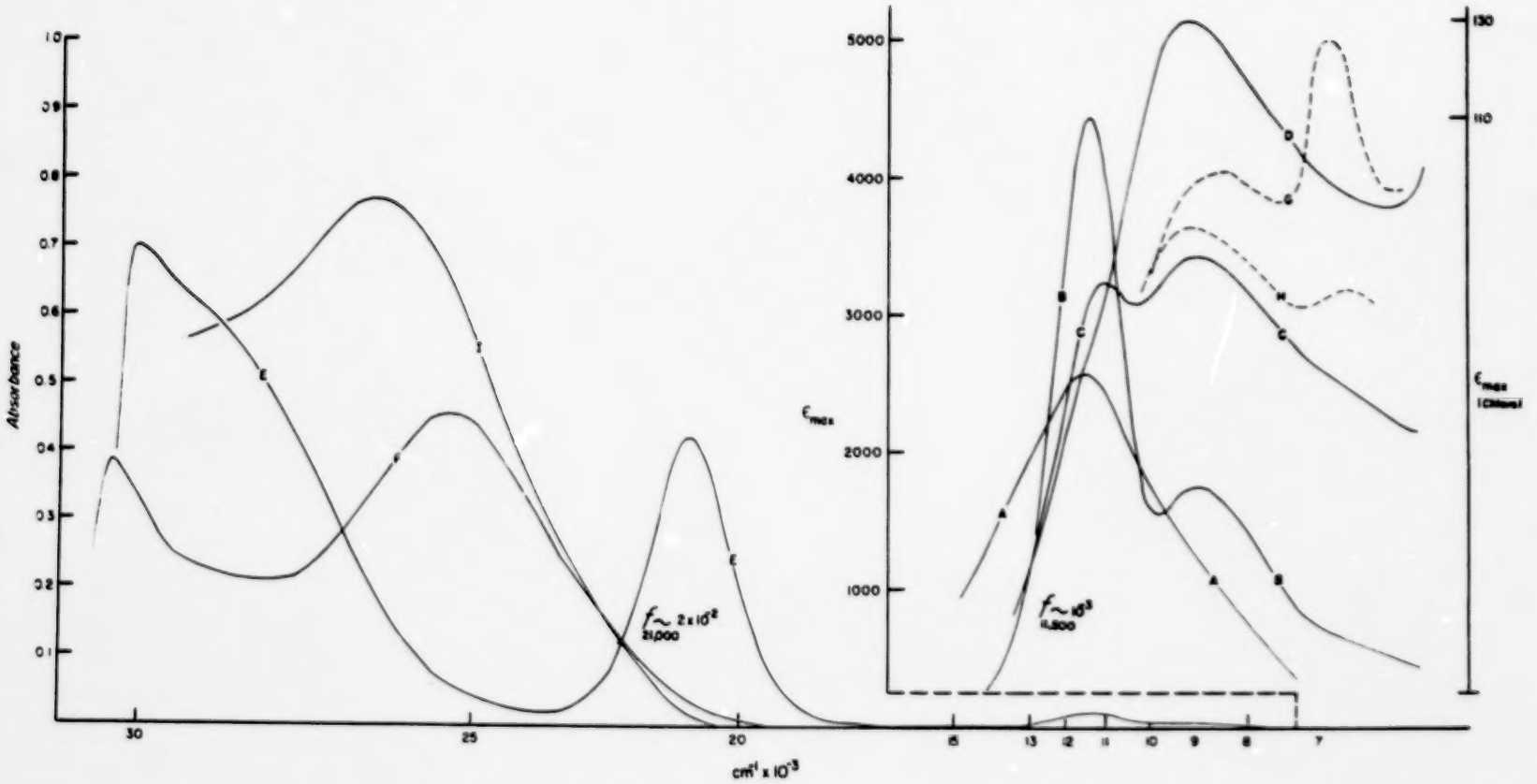

Figure 2 - Spectra of tetrahedral complexes

Cu^{2+} Total	Cl^- / Cu^{2+}
A 8 x 10^{-3} M	2
B "	8
C "	120
D "	610
E 2 x 10^{-4}	26) note change of scale for
F "	12,000) ϵ max

G >4 x 10^{-3}M, acetone solution, 3.3M in HBr.
H 2.5 x 10^{-3}M, 8.2 M HBr (aqueous).
I 2 x 10^{-4}M, $CuCl_2.2H_2O$ in 12 M HCl.

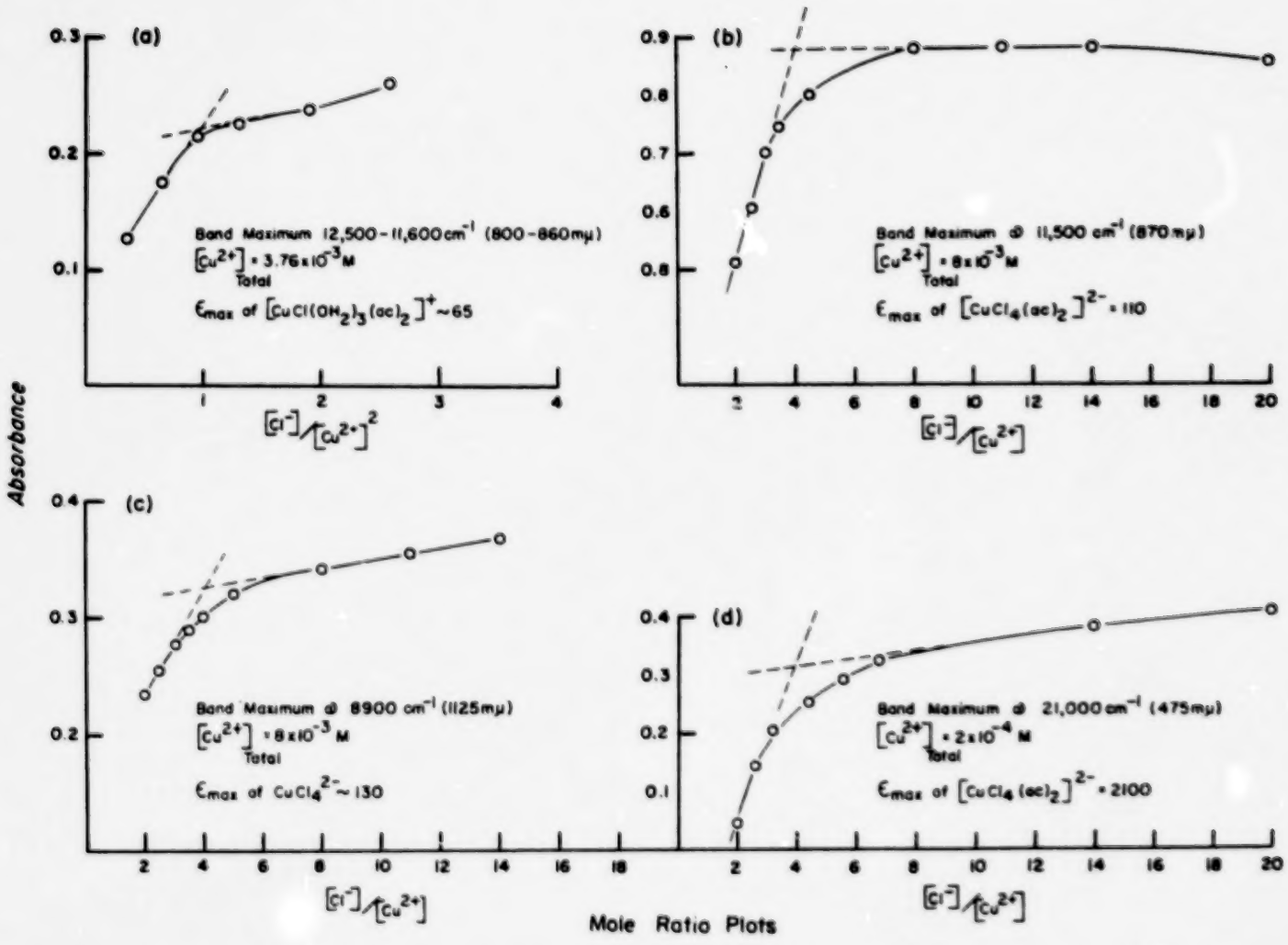
(a)
Band Maximum 12,500 - 11,600 cm⁻¹ (800 - 860 mμ)
[Cu2+] Total = 3.76 x 10⁻³ M
εmax of [CuCl(OH2)3(ac)2]+ ~ 65
[Cl⁻] / [Cu2+]²
(b)
Band Maximum @ 11,500 cm⁻¹ (870 mμ)
[Cu2+] Total = 8 x 10⁻³ M
εmax of [CuCl4(ac)2]2- = 110
[Cl⁻] / [Cu2+]
(c)
Band Maximum @ 8900 cm⁻¹ (1125 mμ)
[Cu2+] Total = 8 x 10⁻³ M
εmax of CuCl4 2- ~ 130
[Cl⁻] / [Cu2+]
(d)
Band Maximum @ 21,000 cm⁻¹ (475 mμ)
[Cu2+] Total = 2 x 10⁻⁴ M
εmax of [CuCl4(ac)2]2- = 2100
[Cl⁻] / [Cu2+]
Absorbance
Mole Ratio Plots

Figure 3 - Mole ratio plots

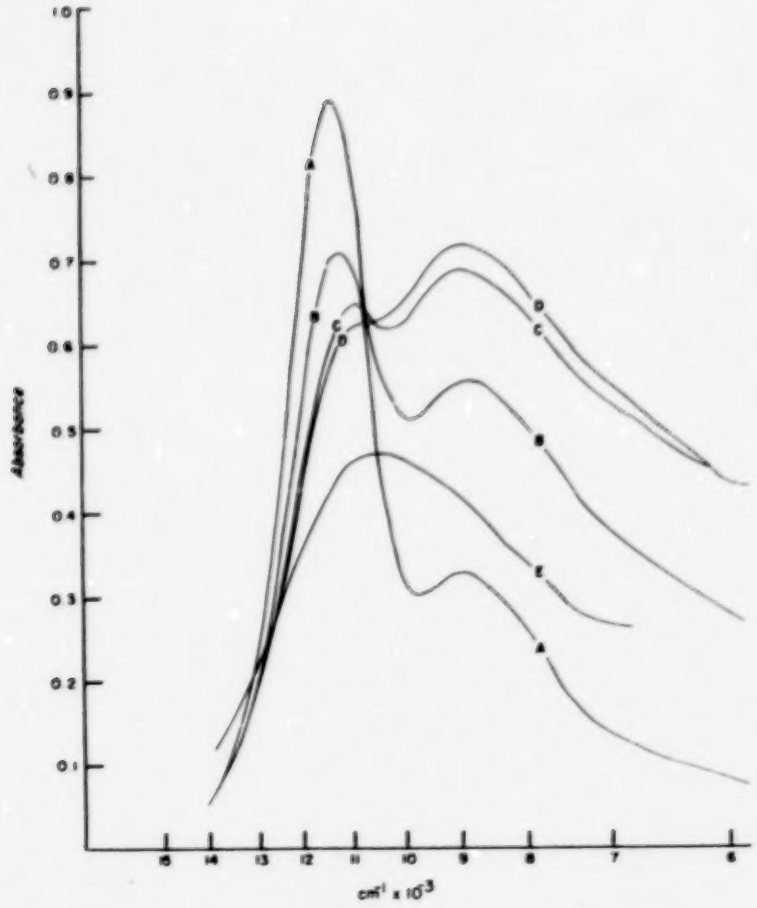

Figure 4 - d-d bands of hexa-, penta-, and tetra-co-ordinated species.

Cu^{2+} Total = 8 x 10^{-3}M

Cl^- / Cu^{2+}

A - 8

B - 62

C - 120

D - 154

E - 2 x 10^{-3}M solution of $CuCl_2.2H_2O$ in 12 M HCl

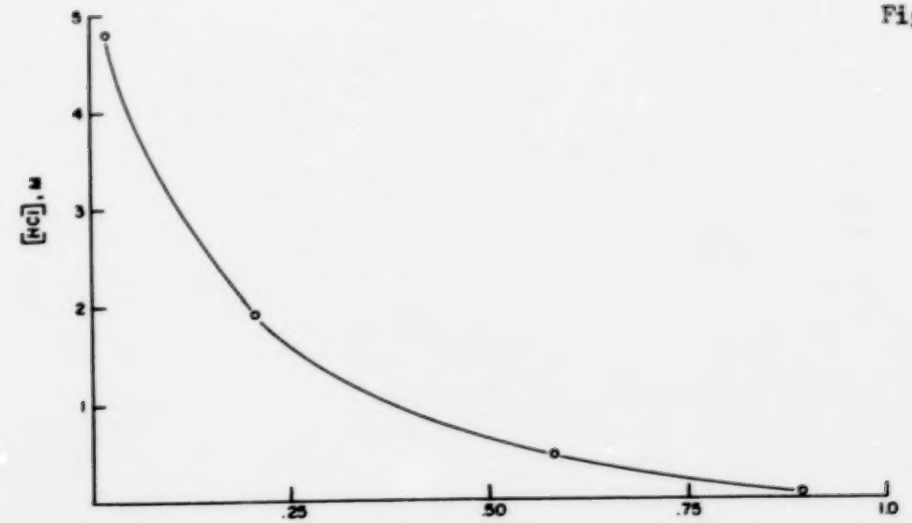

Figure 5 - Fraction of total copper present as $CuCl_4(ac)_2^{2-}$.